Technical Report IRRP-95-5
September 1995

US Army Corps of Engineers
Waterways Experiment Station

Installation Restoration Research Program

Transformation of 2,4,6-Trinitrotoluene Under Controlled Eh/pH Conditions

by Cynthia B. Price, James M. Brannon, WES
Charolett A. Hayes, AScI Corporation

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Prepared for Headquarters, U.S. Army Corps of Engineers

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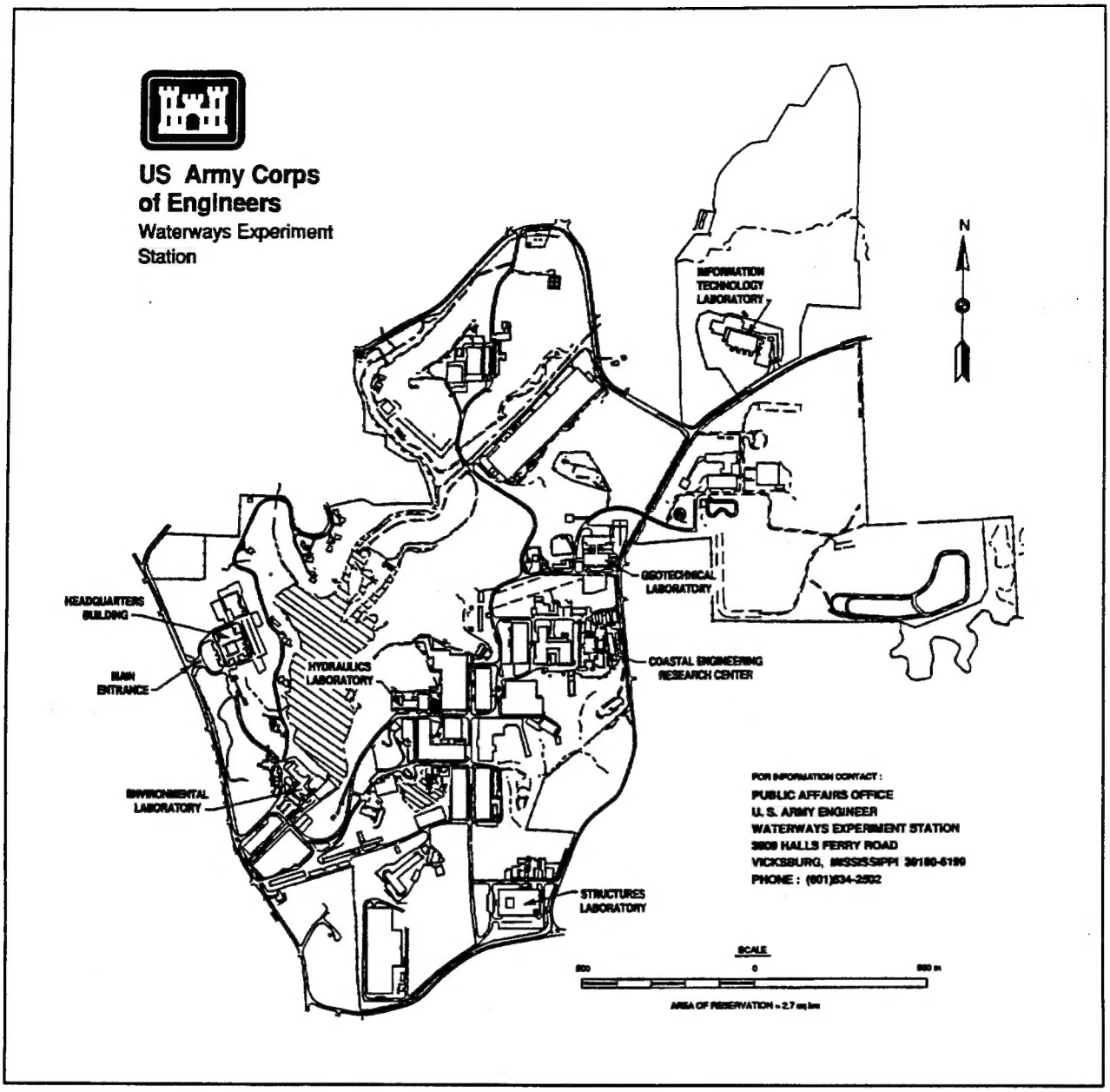
Final report

Approved for public release; distribution is unlimited

Prepared for U.S. Army Corps of Engineers
Washington, DC 20314-1000



Waterways Experiment Station Cataloging-in-Publication Data

Price, Cynthia B.

Transformation of 2,4,6-trinitrotoluene under controlled Eh/pH conditions / by Cynthia B. Price, James M. Brannon, Charolett A. Hayes ; prepared for U.S. Army Corps of Engineers.

29 p. : ill. ; 28 cm. -- (Technical report ; IRRP-95-5)

Includes bibliographic references.

1. Nitrotoluene -- Analysis. 2. Groundwater -- Quality. I. Brannon, James M. II. Hayes, Charolett A. III. United States. Army. Corps of Engineers. IV. U.S. Army Engineer Waterways Experiment Station. V. Installation Restoration Research Program. VI. Title. VII. Series: Technical report (U.S. Army Engineer Waterways Experiment Station) ; IRRP-95-5.

TA7 W34 no.IRRP-95-5

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Preface

The studies reported herein were conducted by the Environmental Laboratory (EL), U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, MS. The research was conducted under the Environmental Quality Basic Research Program. Dr. M. John Cullinane, WES, was the Program Manager.

Personnel who cooperated in the execution of the study and preparation of this report included Ms. Cynthia B. Price and Dr. James M. Brannon, Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), EL; and Ms. Charolett A. Hayes, AScI Corporation. The authors wish to acknowledge Messrs. Scott Towne and Derek Colston for technical assistance. Technical reviews were provided by Drs. Judith C. Pennington and William M. Davis, EPEB; and Mr. Tommy E. Myers, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), EL.

The study was conducted under the direct supervision of Dr. Richard E. Price, Acting Chief, EPEB, and under the general supervision of Mr. Donald L. Robey, Chief, EPED; and Dr. John W. Keeley, Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Bruce K. Howard, EN.

This report should be cited as follows:

> Price, C. B., Brannon, J. M., and Hayes, C. A. (1995). "Transformation of 2,4,6-trinitrotoluene under controlled Eh/pH conditions," Technical Report IRRP-95-5, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

1 Introduction

The explosive 2,4,6-trinitrotoluene (TNT) is widely used and has been manufactured for many decades in the United States. Manufacturing processes have generated wastewaters containing as much as 100 mg of TNT per liter (Palazzo and Leggett 1986). Former disposal practices have resulted in contamination of soil and groundwater at a large number of active and inactive munition sites. The presence of TNT in high concentrations presents serious environmental problems. TNT and some of its transformation products are toxic to fish and other aquatic organisms (Won, Heckly, and Hoffsommer 1974; Nay, Randall, and King 1974). Soils contaminated with TNT inhibit plant growth (Palazzo and Leggett 1986; Folsom et al. 1988; Cataldo et al. 1990). Movement of TNT into aquifers can also adversely affect drinking water supplies.

The processes controlling the transformation and mobility of TNT in soils are not well understood. Previous studies have shown that TNT is subject to transformation (McCormick, Feeherry, and Levinson 1976; Kaplan and Kaplan 1982; Pennington and Patrick 1990; Pennington et al. 1992). Ainsworth et al. (1993) reported that both abiotic and biotic transformations occurred in soils. They postulated that only a subset of TNT sorption sites are active in TNT transformation. Reduction of TNT has been reported in both oxidized and reduced systems (McCormick, Feeherry, and Levinson 1976; Pennington and Patrick 1990). Reduction of nitro groups to amino groups by Fe^{+2} sorbed to surfaces has been shown to occur by Heijman et al. (1995) for nitroaromatics other than TNT.

The objective of this study was to determine the effects of redox potential (Eh) and pH on TNT transformation in soil. Soil components responsible for the reduction were also identified.

2 Materials and Methods

Soil Collection

A predominantly clay (49 percent) agricultural surface soil from the Mississippi River floodplain was used. The soil was classified as very fine, montmorillonite, nonacid, thermic Vertic Haplaquept (U.S. Soil Conservation Service classification) and designated Yokena Clay. The soil was air-dried, ground, and sieved through a 2-mm (0.08-in.) sieve. The sieved samples were thoroughly mixed, transferred to polyethylene containers, sealed, and stored at room temperature.

Eh-pH Incubation

Tests were conducted in 2,800-mL (0.74-gal) Fernbach flasks. Organic matter (0.5-percent w/w) was added as an energy source for oxygen-consuming microorganisms. The organic matter obtained from the Atchafalaya Basin, Louisiana, was air-dried and ground to a powdery consistency in a roller mill before use. Sufficient distilled deionized water was added to the flasks to produce a water-to-solids ratio of 18:1. The water-soil slurries were kept in suspension by magnetic stirring and were maintained at room temperature that averaged 30.5 °C $\pm$ 1.02.

Control of Eh and pH in the slurries was maintained using the methods developed by Patrick, Williams, and Moraghan (1973) with some modifications (Brannon 1983). The Eh was monitored by platinum and Ag-AgCl electrodes connected to a pH-millivolt meter (Beckman Instruments, Fullerton, CA) (Figure 1). The desired Eh was set on a meter relay (Currier and Roser, New Orleans, LA), which, by activating an aquarium air pump when the set point was reached, prevented the Eh from falling below the preset value. When the suspension was oxidized to the desired Eh, the meter relay automatically switched off the air pump. To help maintain anaerobic conditions, nitrogen gas was flushed through the system at a rate of approximately 15 mL/min (0.24 gal/hr). A combination pH electrode connected to a separate meter monitored pH. The desired pH was maintained by injecting 1.0-N HCl or 1.0-N NaOH via a syringe through a serum cap into the suspension. The soil

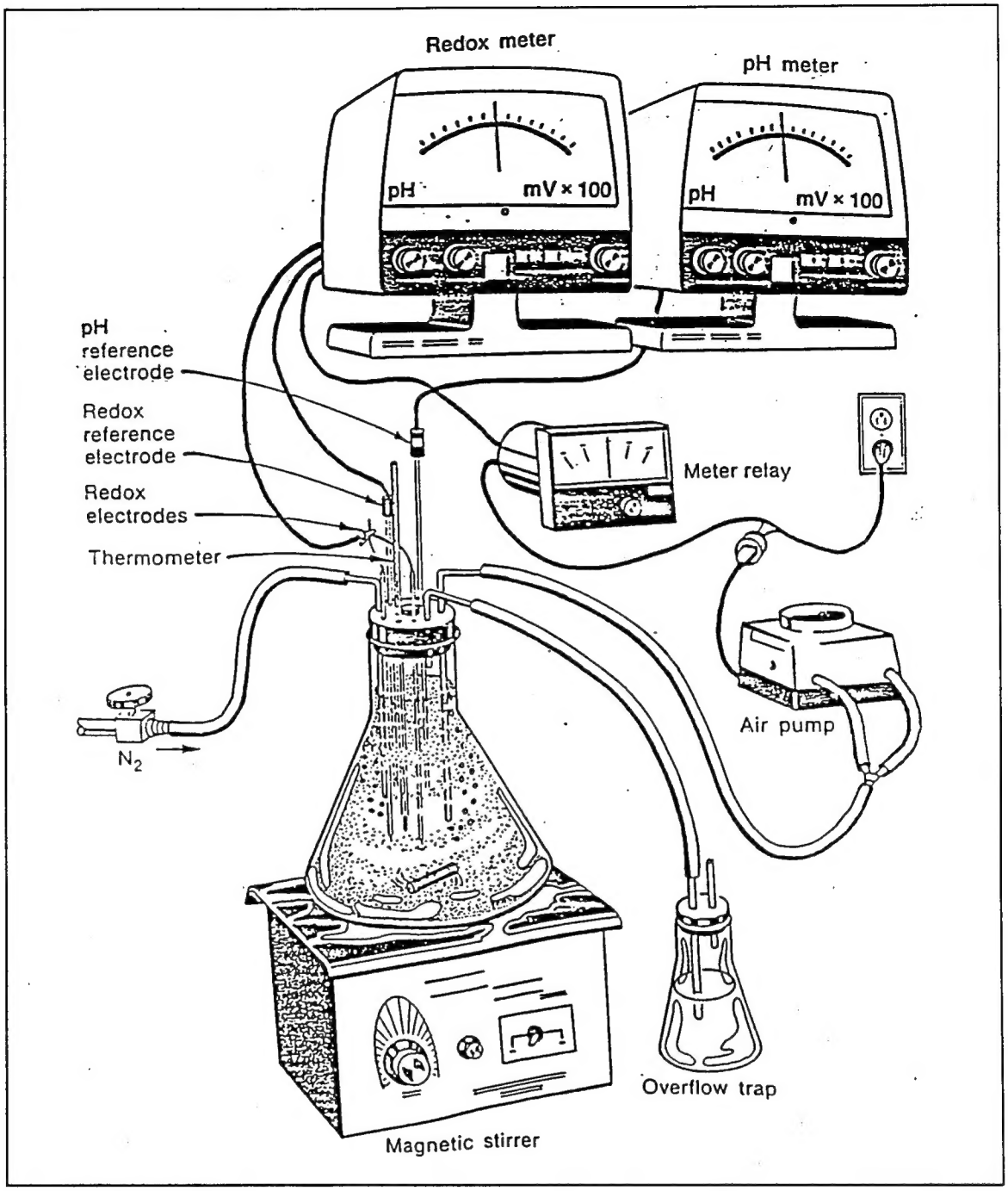

Figure 1. System used to control Eh and pH over time

suspensions were allowed to incubate and stabilize (approximately 2 weeks depending upon the Eh) at the chosen Eh-pH levels before the addition of TNT.

The study consisted of duplicate tests at four Eh levels, +500, +250, 0, and -150 mV, and four pH values, 5.0, 6.0, 7.0, and 8.0, or 32 experimental units.

Four separate sets of test soil-water suspensions incubated at four Eh levels, +500, +250, 0, and -150 mV were used. Tests at each Eh level were incubated in duplicate with each of four pH levels, 5.0, 6.0, 7.0, and 8.0.

Following the initial incubation period to stabilize the pH and Eh, 1 mL (0.0338 oz) of methanol containing 15-mg TNT (2.31 grains) was added to the soil suspension in each flask (equivalent to 100 µg of TNT per gram (0.044 grains/oz) of soil). All flasks were covered with aluminum foil prior to spiking to prevent photodecomposition of the added TNT. Slurry samples were withdrawn at 1, 4, 9, and 14 days after addition of TNT via a syringe through the serum cap. The samples were dispensed into 25-mL (0.845-oz) glass centrifuge tubes and centrifuged at 1,000 RCF for 45 min to separate the aqueous and solid phases. Water samples were analyzed for TNT and its transformation products, which included 1,3,5-trinitrobenzene (TNB), 1,3-dinitrobenzene (DNB), 4-amino-2,6-dinitrotoluene (4A-DNT), 2-amino-4,6-dinitrotoluene (2A-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 3,5-dinitroanaline (DNA), 2,6-diamino-4-nitrotoluene (2,6-DANT), and 2,4-diamino-6-nitrotoluene (2,4-DANT). Analyses were performed according to EPA SW-846 Method 8330 (U.S. Environmental Protection Agency (EPA) 1990). Following 14 days of incubation, the flasks were sampled for both water and soil. The water samples were obtained as described above. The flask contents were allowed to settle and the remaining aqueous phase decanted. The soils were then centrifuged to remove the remaining water, and a homogenized subsample was taken for analysis. The soils were analyzed for the same parameters as the waters with the addition of total tetranitroazoxytoluenes.

Mass balance of TNT was determined in additional Eh/pH reactors using uniformly ring-labeled TNT ((^{14}C)TNT) (New England Nuclear Research Products, Boston, MA). Tests were run in duplicate at both +250 mV and -150 mV at pH 7. A bubble trap containing 1 N KOH was added to each flask to trap CO_2. All tests were set up identically to the Eh/pH incubations with unlabeled TNT. The total incubation period was 14 days. The KOH traps were sampled each day, and the water and soil were sampled on Day 14. Radiolabeled TNT and transformation products in the aqueous phase and trapped radiolabeled CO_2 were determined by counting 1 mL of water or KOH in 15-mL Ultima Gold Liquid Scintillation Cocktail (Packard Instruments, Meridan, CT) on a Packard Tricarb 2500 TR Liquid Scintillation (LS) Counter (Packard Instruments, Meridan, CT). The soil was analyzed for radiolabeled products by complete combustion in a Model 307 Packard Sample Oxidizer (Packard Instruments, Meridan, CT). Oxidized carbon was trapped as CO_2 in Carbo-Sorb and Permaflour Liquid Scintillation Cocktail (Packard Instruments, Meridan, CT) and assayed as described previously.

Clays and Cation Effects

The ability of selected clays and cations to mediate transformation of TNT was investigated under both aerobic and anaerobic conditions. The clays tested were montmorillonite and kaolinite. The cations Fe^{+2} and Mn^{+2} were tested because they commonly occur in soils and sediments and were likely to affect the abiotic transformation of TNT. Two hundred mls (6.76 oz) of distilled, deionized water was added to 250-mL (8.45-oz) amber bottles with sufficient iron oxide (Fe_2O_3), manganese dioxide (MnO_2), aluminum hydroxide ($Al(OH)_3$), montmorillonite, or kaolinite to yield a solution concentration of 100 mg/ℓ (5.84 grains/gal) of each component. The amount of component added was selected to minimize sorption yet allow transformations to be readily observed. Each treatment was spiked to give a solution concentration of 50 mg/ℓ (2.92 grains/gal) of TNT. Each treatment was conducted in triplicate. A control of distilled deionized water and TNT alone was also run. After spiking, the bottles were placed on a reciprocating box shaker at 120 excursions per min and sampled at 24 and 72 hr. At each sampling period, 10 mls (0.338 oz) of solution was removed and frozen until analysis. The pH of each solution was checked at each sampling time.

The MnO_2 was prepared, washed, and dried as described by Loganathan and Burau (1973). Ferric oxyhydroxide was prepared by hydrolysis of ferric chloride in a dilute sodium hydroxide solution (pH = 12). The resulting red precipitate was repeatedly washed with distilled water until the supernatant pH reached 7.0. The manganese and iron oxides were oven-dried at 45 °C, ground with an agate mortar and pestle to 140 mesh, and stored in an airtight container at room temperature. Analysis of the Fe and Mn precipitates by X-ray diffraction showed that both were amorphous (no rigid crystalline structure).

Ferrous (Fe^{+2}) chloride and manganous (Mn^{+2}) chloride were tested alone under anaerobic conditions. Ferrous chloride was also tested in the presence and absence of kaolinite and montmorillonite. All test preparations and sampling used deoxygenated distilled deionized water under a nitrogen atmosphere. The nitrogen atmosphere was necessary to prevent precipitation of the reduced iron and manganese as their respective oxides. The tests containing the ferrous chloride and the manganous chloride were sampled for Fe^{+2} and Mn^{+2} concentrations prior to TNT spiking and at each sampling period to verify that oxidation and removal of these components by precipitation had not occurred.

The TNT spike for the Fe^{+2}, Mn^{+2}, kaolinite + Fe^{+2}, and montmorillonite + Fe^{+2} treatments was somewhat higher (64 mg/ℓ) (3.74 grains/gal) than the spike for the other treatments because sample was withdrawn for Fe^{+2} analyses prior to TNT spiking.

3 Results and Discussion

Experimental Variability

Mean coefficients of variation (CV) for parameters measured during the Eh/pH incubations and TNT transformation investigations are summarized in Table 1. Experimental variation included variation between replicates, variation because of sample handling, and analytical variability; this was 20.2 percent for TNT and generally less than 40 percent for the transformation products measured in the Eh/pH incubations and less than 8 percent for all parameters measured in the TNT transformation investigations.

Table 1
Mean Coefficients of Variation for Compounds Measured During Eh/pH Incubations and TNT Transformation Investigations

	Eh/pH Incubations						
	TNT	TNB	4A-DNT	2A-DNT	2,4-DNT	2,6-DANT	2,4-DANT
Soil Slurry	20.2	–	38.1	42.5	–	24.1	34.3
Selected Clays and Cations							
$Al(OH)_3$	7.7	5.1	–	–	6.4	–	–
MnO_2	6.0	4.0	–	–	3.9	–	–
Kaolinite	7.8	4.4	–	–	3.1	–	–
Montmorillonite	6.0	6.6	–	–	7.3	–	–
Fe_2O_3	5.1	2.6	–	–	6.1	–	–
Fe^{+2}	2.9	2.4	–	–	4.5	–	–
Mn^{+2}	2.1	9.5	–	–	7.5	–	–
Mont + Fe^{+2}	3.2	–	–	–	–	–	–
Kaolinite + Fe^{+2}	16.8	–	–	–	–	–	–
Water control	7.2	3.4	–	–	3.3	–	–

Eh/pH Incubations

Redox potential and pH of the soil suspensions had a marked effect on TNT transformation and stability. The TNT was not stable at any Eh/pH test combination. Less than 8 percent of the added TNT remained in any treatments. Table 2 shows the total percent mass of TNT remaining in the suspensions (soil and water) after the 14-day incubation. The TNT was most stable at 0 mV and pH 5, where 7.4 percent of added TNT remained (Figure 2).

Table 2
Percentage of TNT Remaining in the Aqueous and Soil Phases 14 Days After Addition of 15 mg TNT

pH	+500 mV	+250 mV	0 mV	-150 mV
5	0.20	1.05	7.4	<0.007
6	0.13	0.25	3.28	<0.007
7	0.09	0.11	<0.007	<0.007
8	0.14	0.06	<0.007	<0.007

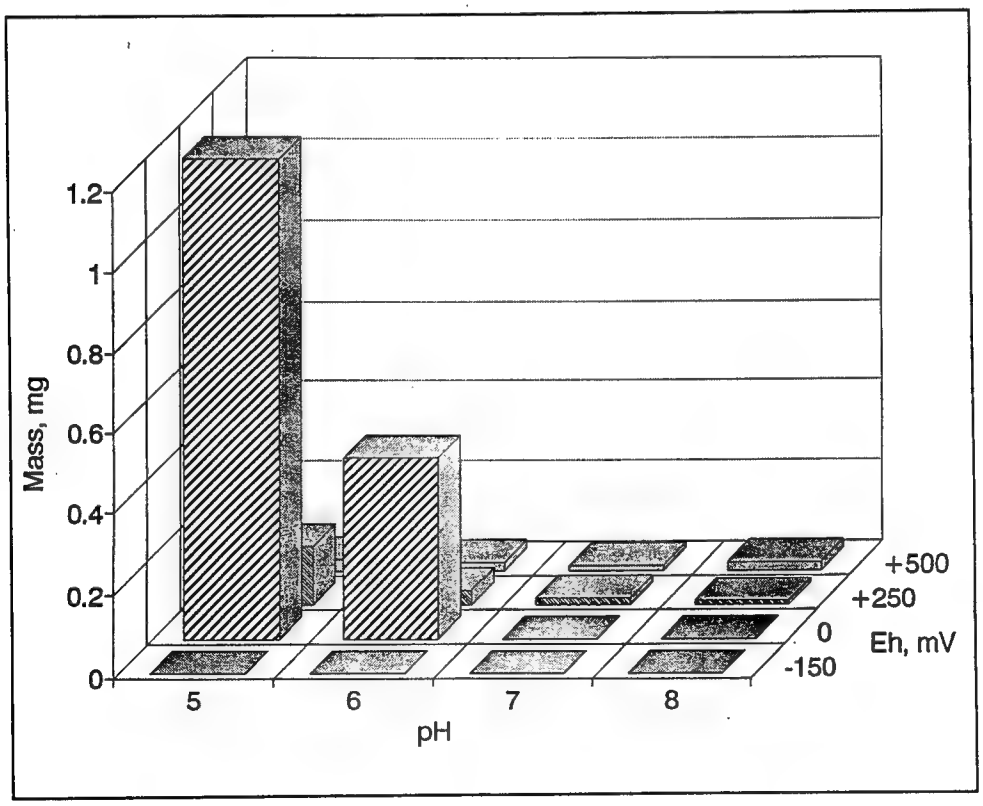

Figure 2. Total mass of TNT remaining (aqueous plus soil phases) 14 days after addition of 15 mg (2.31 grains) TNT at various Eh and pH values

Less TNT was recovered at higher Eh values, and no TNT was recovered at lower Eh values. Under highly reducing conditions, -150 mV, TNT was not present at any pH. Most of the TNT recovered was in the soil (Figure 3). TNT was recovered in the water only at pH 5 in the 0-mV system (Figure 3). These results indicate that TNT persisted in the system only under moderately reducing (0-mV) and oxidizing conditions at pH 6 or below.

At pH 6, 7, and 8, essentially all added TNT disappeared from solution after 1 day of incubation (Figure 4). TNT persisted longest in the 0-mV treatment at pH 5. These results indicate that TNT added to uncontaminated soil will not persist in solution under a wide range of redox potential and pH. The removal of TNT from the system by soil is most rapid and complete under highly reducing (Eh = -150 mV) conditions. Similar results were also noted by Folsom et al. (1988), who reported that the percent recovery of TNT in soils tended to decrease as soil pH increased.

The transformation products produced were strongly related to the Eh of the soil system. Following 1 day of incubation, the transformation products 4A-DNT and 2A-DNT were present in solution at all Eh/pH combinations (Figure 5). Other products, 2,6-DANT and 2,4-DANT, were present in the solution phase of the 0- and -150-mV tests only. No other products were detected. At +500 mV and +250 mV, only 4A-DNT and 2A-DNT were present in solution. However, at 0 mV, 2,6-DANT and 2,4-DANT began to appear in solution, especially at pH 8.0. Under highly reduced conditions, -150 mV, 2,6-DANT and 2,4-DANT were present at all pHs, with the highest concentrations occurring at pH 6, 7, and 8 (Figure 5). McCormick, Feeherry, and Levinson (1976) reported that the nitro groups on the TNT molecule are reduced in both aerobic and anaerobic systems and that, depending upon how reduced the system was, either one, two, or three of the nitro groups may be reduced to aminos. The data in this study show that rapid reduction of nitro groups to amino groups is favored under highly reducing conditions (-150 mV). Concentrations of 2,6-DANT and 2,4-DANT increased in the -150-mV treatment compared with the 0-mV treatment with a corresponding decrease in concentrations of 2A-DNT and 4A-DNT. This suggests that the transformation of TNT is a stepwise reduction process progressing from amination of a single nitro group to two nitro groups.

The pattern of 2,6-DANT and 2,4-DANT being present under reducing conditions (0 mV and -150 mV) and absent under oxidized conditions (+500 mV and +250 mV) following 1 day of incubation generally persisted over the 14-day study period. At +500 and +250 mV, concentrations of 4A-DNT and 2A-DNT generally peaked at Day 4 at all pHs or remained constant and persisted over the 14 days of incubation (Figures 6 and 7). TNT was no longer present in solution at Day 4 except at pH 5.0 in the +250-mV treatment; 2,6-DANT and 2,4-DANT were either not detected or present in low concentration in the +500- or +250-mV treatments.

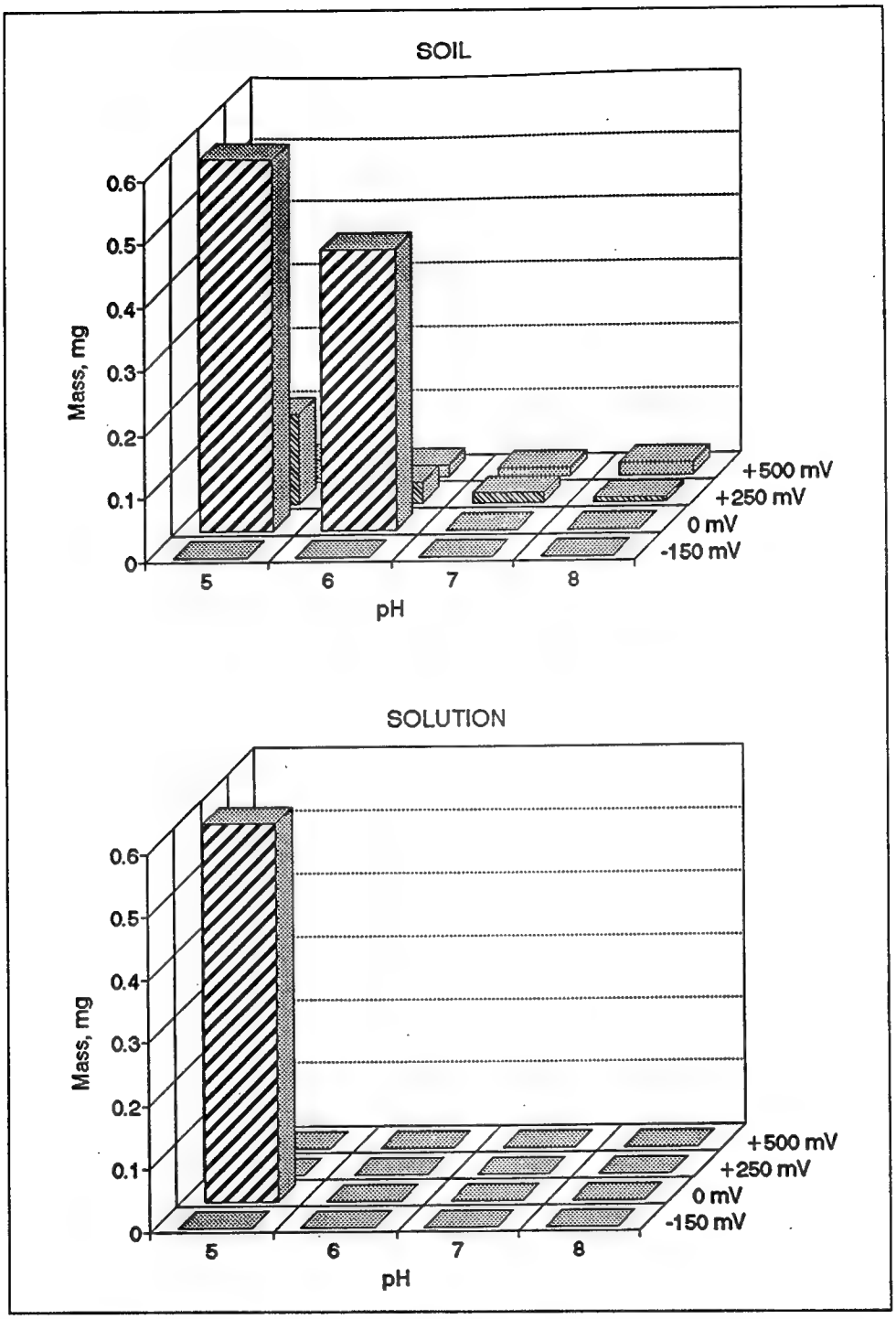

Figure 3. Mass of TNT remaining (aqueous plus soil phases) 14 days after addition of 15 mg (2.31 grains) TNT at various Eh and pH values

In the 0-mV treatment, higher initial concentrations of amino compounds were detected (Figure 8). At pH 5 and 6, concentrations of 2A-DNT and 4A-DNT had peaked by Day 1. At pH 7 and 8, concentrations of 2A-DNT and 4A-DNT peaked at Day 4. Concentrations of 2,6-DANT and 2,4-DANT

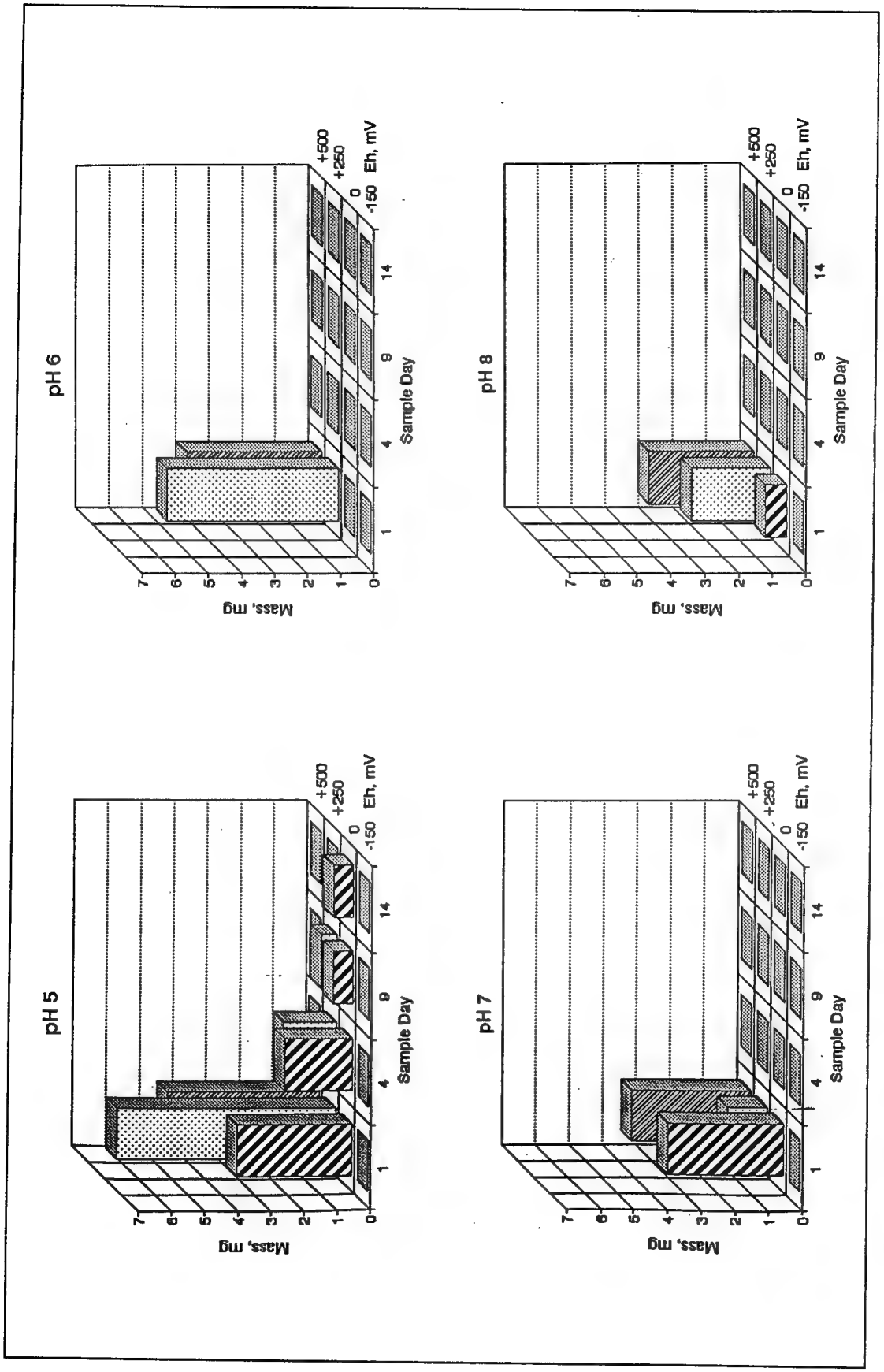

Figure 4. Aqueous mass of TNT over time at each pH level

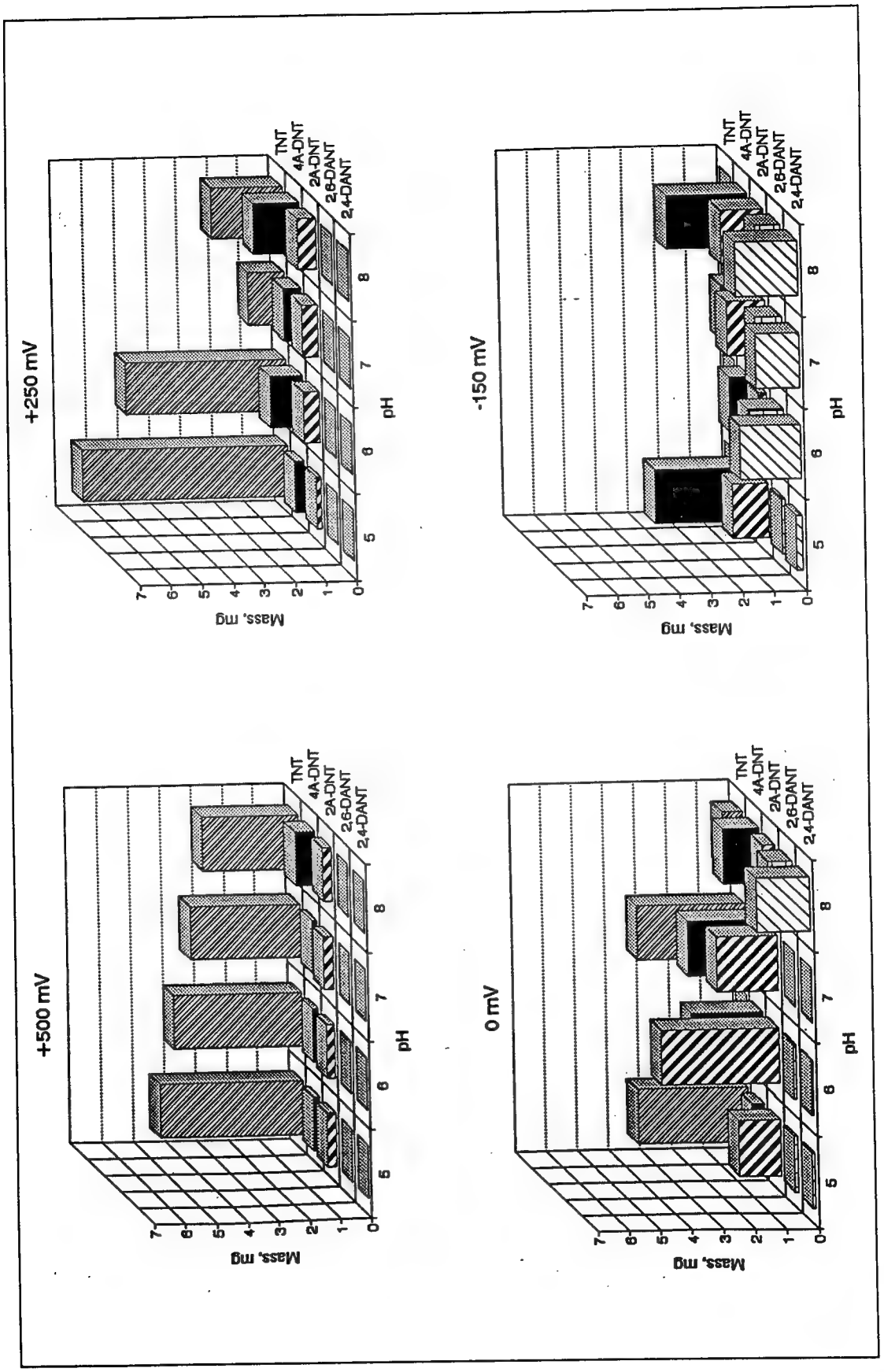

Figure 5. Aqueous mass of TNT and transformation products following 1 day of incubation

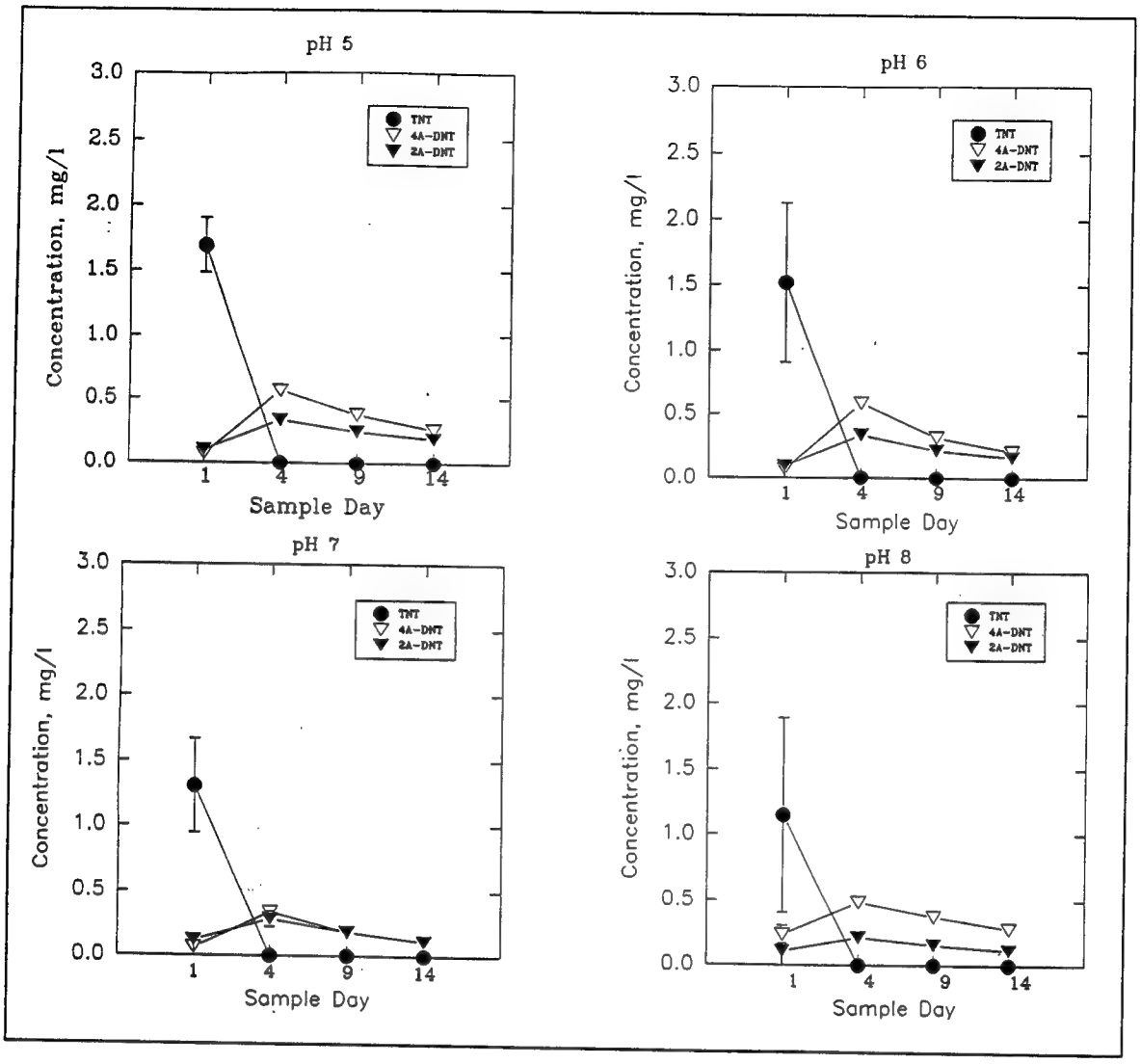

Figure 6. TNT and its transformation products in solution at each pH over time at +500 mV

generally increased slightly or remained relatively constant over time and were present at higher concentrations at 0 mV than at +250 mV.

Disappearance of TNT and appearance of its transformation products was most rapid at -150 mV (Figure 9). Concentrations of 2A-DNT, 4A-DNT, 2,6-DANT, and 2,4-DANT generally peaked at Day 1 except at pH 5 where 2,6-DANT and 2,4-DANT concentrations increased. TNT was not detected in solution at any sampling time in any pH treatment.

Results of solution analyses indicate that as Eh decreased, reduction of nitro groups on TNT to amino groups became more rapid and progressed from one to two nitro groups. Soil sampling and analysis at 14 days confirmed these results (Figure 10). TNT was not present in the soils, and degradation products were present only at pH 5 in the -150 mV test. These results indicate that

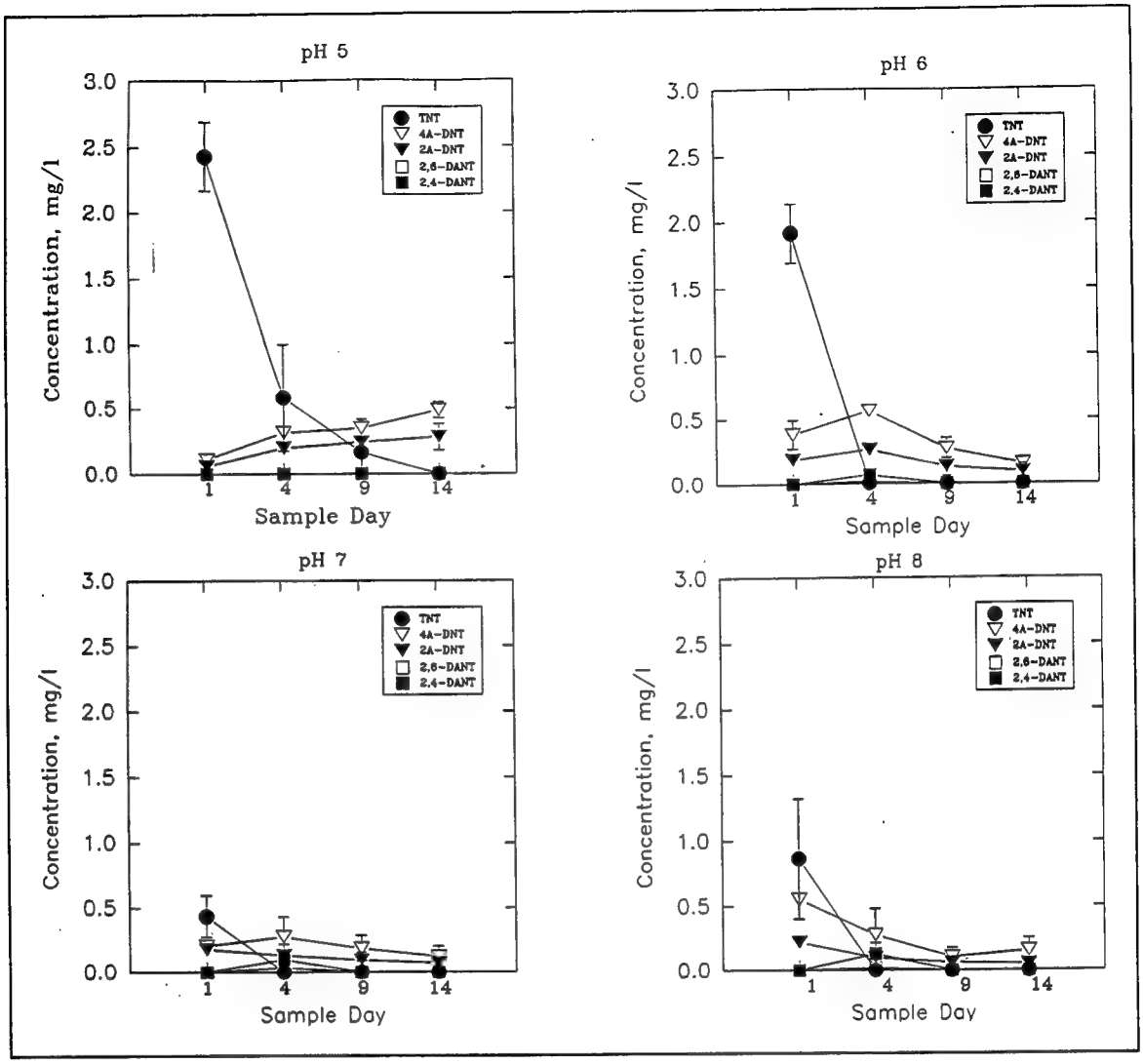

Figure 7. TNT and its transformation products in solution at each pH over time at +250 mV

TNT in a highly reduced system will not persist as the parent compound or its transformation products. Higher concentrations of TNT and its degradation products were generally found as pH decreased except for isolated exceptions such as pH 8 in the +500-mV treatment. Percent recovery data, including both the soils and water, for TNT following 14 days of incubation (Figure 11) further illustrated the impact of pH and Eh on TNT. Where TNT persisted, recovery generally increased as pH decreased. Recovery trends were not as clear for Eh except at pH 8 where recovery decreased as Eh decreased. The most pronounced finding was the disappearance of all TNT at -150 mV, regardless of the pH.

As presented earlier in Figure 3, TNT was not found in either the soil or solution phase of the -150-mV tests by the end of the 14-day incubation test run. The only transformation products in the soils were found at pH 5 and consisted of 4A-DNT, 2A-DNT, 2,6-DANT, and 2,4-DANT. The waters

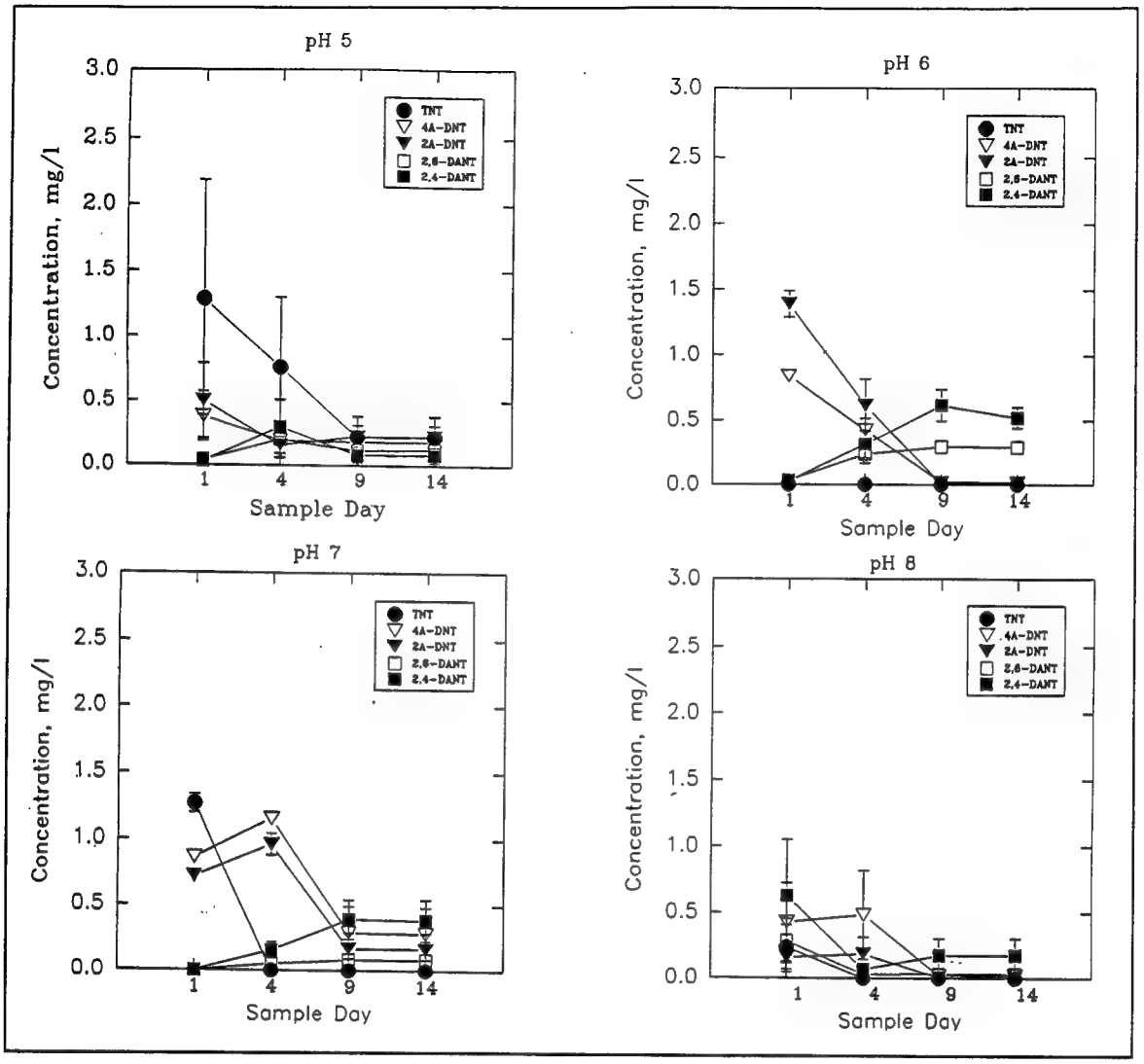

Figure 8. TNT and its transformation products in solution at each pH over time at 0 mV

contained 4A-DNT, 2,6-DANT, and 2,4-DANT at pH 5 and 8. The highly reduced conditions of this treatment promoted complete transformation of TNT and also disappearance of the transformation products investigated in this study (Figure 9).

Mass Balance for Eh/pH Incubations

Results showed most of the radiolabeled carbon was present in the Eh/pH reactor vessels. In the +250-mV test, total recovery of radiolabled carbon was 113 percent. The additional percentage was probably due to spiking error. Of this total, 83 percent of the radiolabel was present in the soil, 31 percent in the water, and 2.7 percent was mineralized as CO_2. The -150-mV tests showed

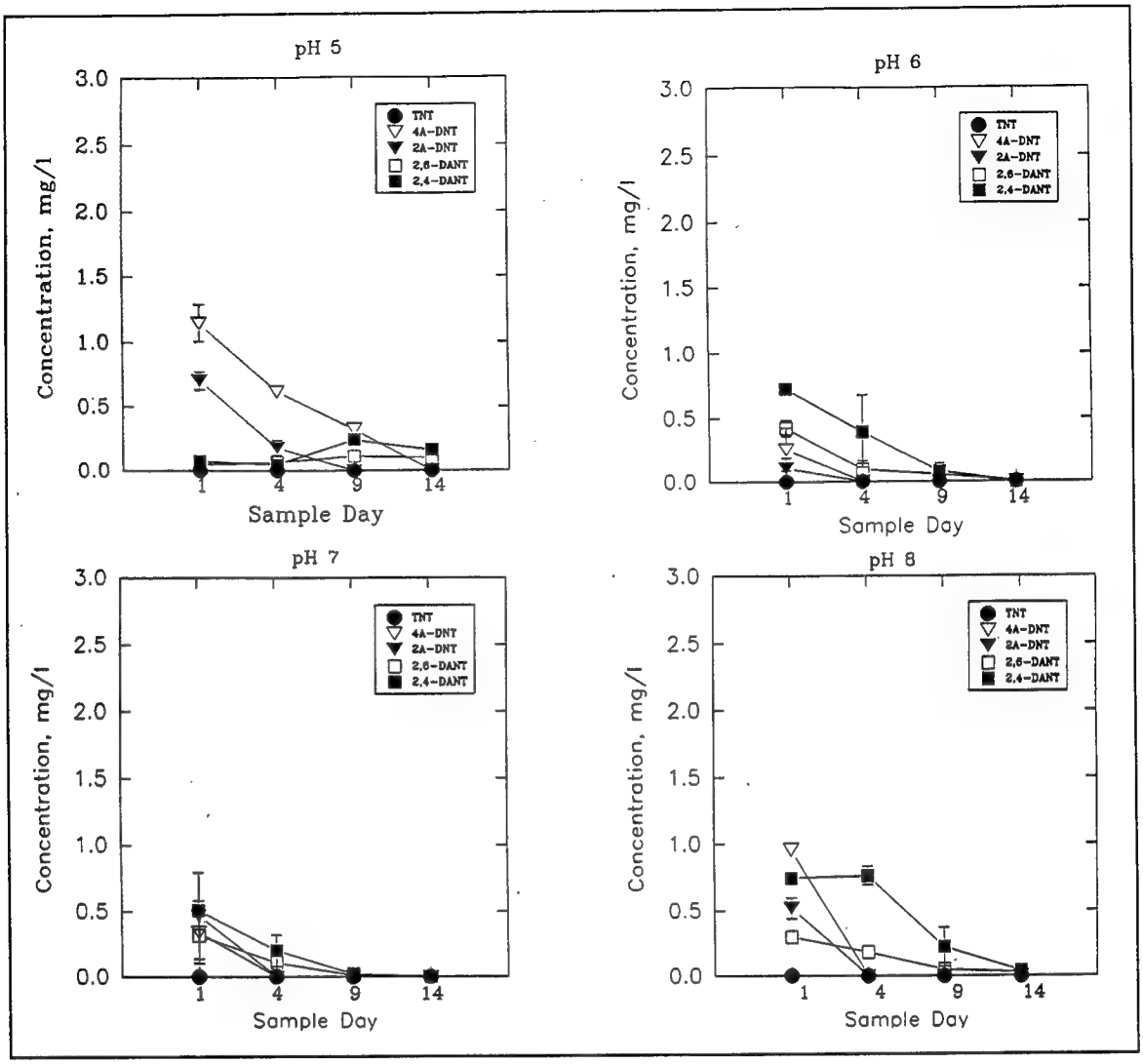

Figure 9. TNT and its transformation products in solution at each pH over time at -150 mV

similar results. Total recovery of the radiolabel for this test was 92 percent. The soil contained 82 percent of the radiolabel, with the water containing 9.6 percent and the KOH traps 0.09 percent. These data support the conclusion that low percent recovery in the initial tests was a result of the degradation products being bound to the soil in unmeasured and perhaps unextractable forms.

TNT Transformations Mediated by Soil Components

The pH changed by less than 10 percent between the 24- and 72-hr sampling period (Table 3). Addition of Fe^{+2} to montmorillonite and kaolinite generally lowered the pH, but not more than one pH unit.

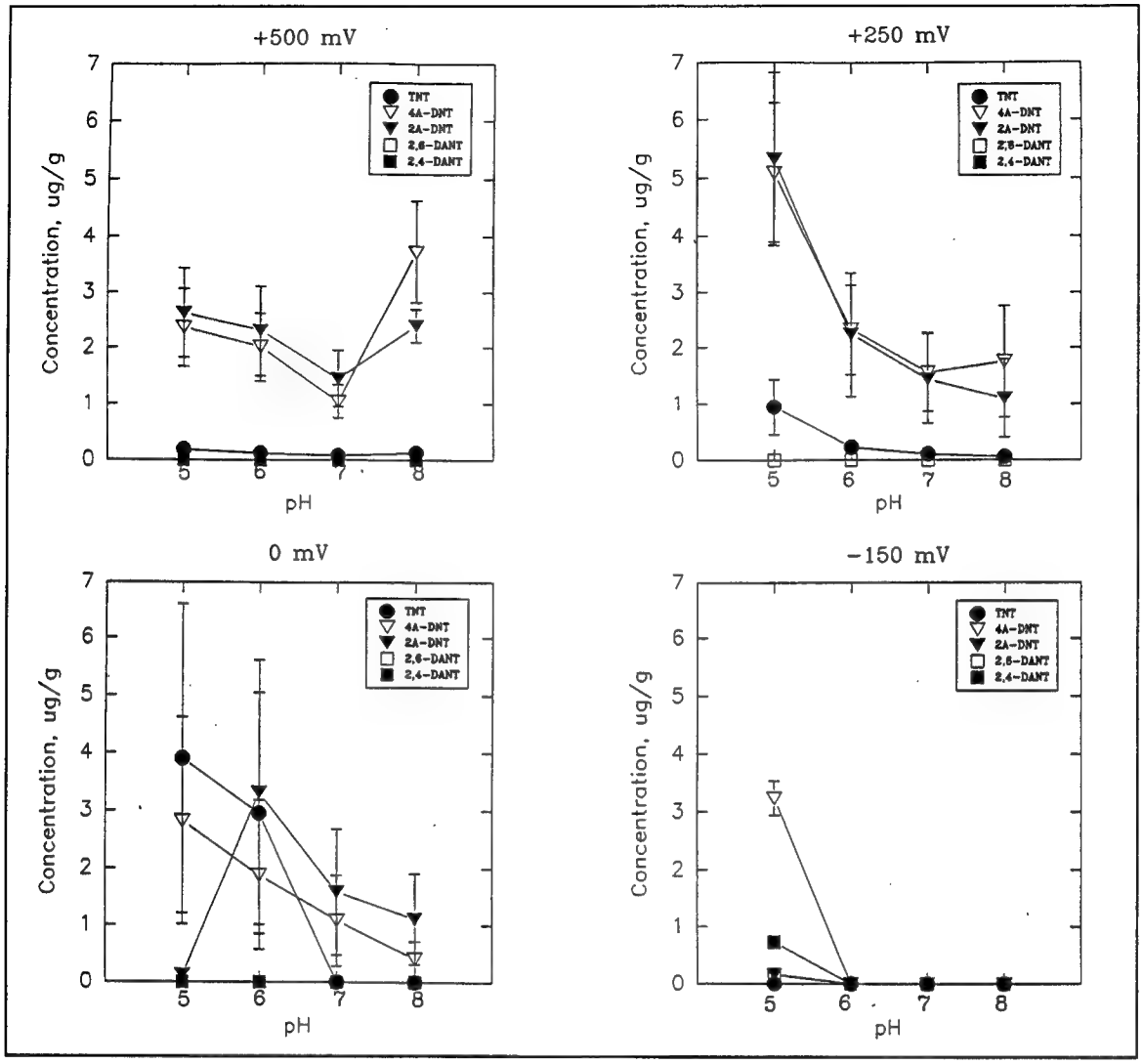

Figure 10. TNT and its transformation products in soil at each pH and Eh 14 days after addition of TNT

No significant disappearance of TNT was noted for any of the treatments with the soil components alone (Table 4). Low amounts of TNB and 2,4 DNT were detected in all but the montmorillonite + Fe^{+2} and kaolinite + Fe^{+2} treatment. However, the concentrations of TNB and 2,4 DNT observed were generally similar to those found in the water control, indicating either presence in the stock solution or formation during the test. The water control showed a decrease in TNT from 46.5 to 44.3 mg/ℓ (2.72 to 2.59 grains/gal) from 24 to 72 hr.

Disappearance of TNT from solution expressed as the concentration of TNT at sampling time over the initial concentration present in the system (C/C_o) was observed in the montmorillonite + Fe^{+2} and kaolinite + Fe^{+2} treatments (Figure 12). TNT disappearance was rapid in these treatments, with approximately 90 percent of the added TNT lost within 24 hr. TNT showed no

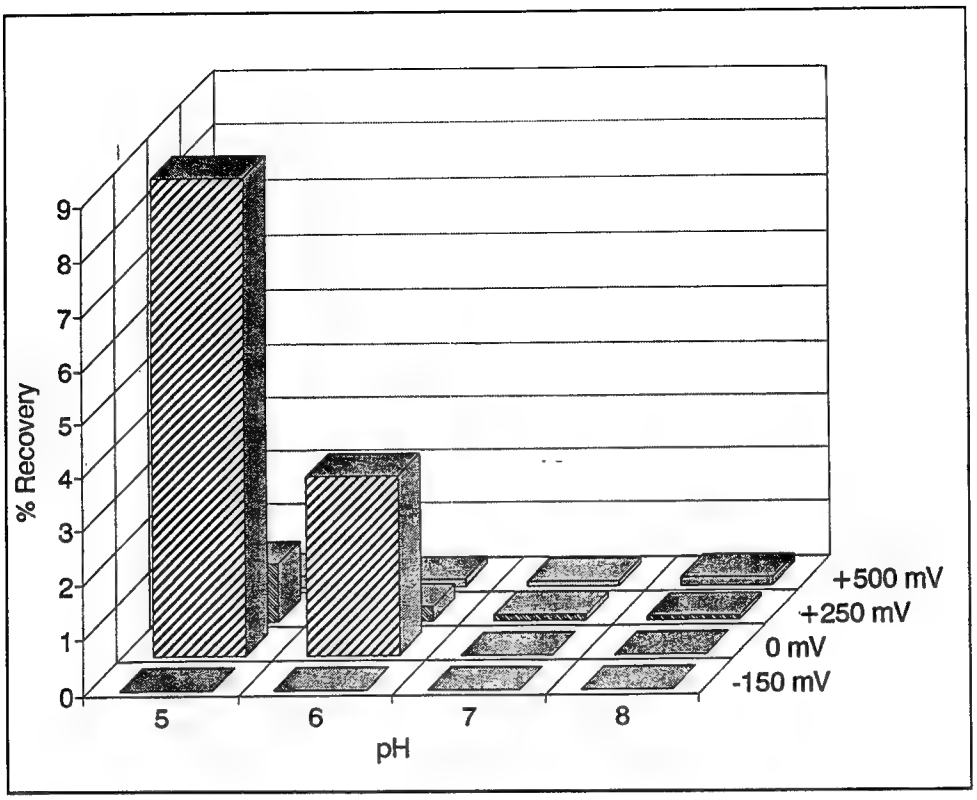

Figure 11. Percent recovery of TNT totaling both the soil and water after the 14-day sampling period

Table 3
Solution pH of the Various Water-Soil Component Mixtures During Testing

Treatment	Time, hr	
	24	48
$Al(OH)_3$	6.04	6.13
MnO_2	5.39	5.99
Kaolinite	5.86	5.86
Montmorillonite	5.28	5.64
Fe_2O_3	5.76	6.28
Fe^{+2}	4.80	4.50
Mn^{+2}	7.20	7.20
Montmorillonite + Fe^{+2}	5.00	4.80
Kaolinite + Fe^{+2}	5.00	4.80
Water control	7.30	7.00

Table 4
Concentrations of TNT in Various Water-Soil Component Mixtures During Testing

Treatment	TNT Concentration, mg/ℓ		TNB Concentration, mg/ℓ		2,4-DNT Concentration, mg/ℓ	
	24 hr	72 hr	24 hr	72 hr	24 hr	72 hr
$Al(OH)_3$	48.9 (2.67)	44.1 (1.53)	0.028 (0.001)	0.028 (0.0003)	0.029 (0.0009)	0.026 (0.001)
MnO_2	46.6 (0.14)	41.7 (2.47)	0.031 (0.0009)	0.037 (0.0007)	0.03 (0.0006)	0.026 (0.0007)
Kaolinite	45.5 (3.08)	45.3 (0.99)	0.029 (0.0009)	0.029 (0.0006)	0.029 (0.0007)	0.024 (0.0003)
Montmorillonite	45.2 (1.37)	46.4 (1.81)	0.029 (0.001)	0.032 (0.001)	0.027 (0.0007)	0.026 (0.002)
Fe_2O_3	42.3 (1.47)	47.1 (1.13)	0.028 (0.0003)	0.031 (0.0006)	0.029 (0.0006)	0.027 (0.001)
Fe^{+2}	63.1 (0.61)	60.4 (1.50)	0.049 (0.0003)	0.048 (0.001)	0.036 (0.021)	0.032 (0.032)
Mn^{+2}	60.0 (0.59)	61.6 (0.93)	0.052 (0.002)	0.055 (0.004)	0.034 (0.02)	0.031 (0.018)
Montmorillonite + Fe^{+2}	6.64 (0.45)	6.48 (0.19)	<0.02	<0.02	<0.02	<0.02
Kaolinite + Fe^{+2}	7.16 (0.69)	7.41 (0.74)	<0.02	<0.02	<0.02	<0.02
Water control	46.5 (2.92)	44.3 (0.92)	0.028 (0.0003)	0.031 (0.0006)	0.027 (0.0003)	0.026 (0.0007)

Note: Parentheses represent standard error of the mean.

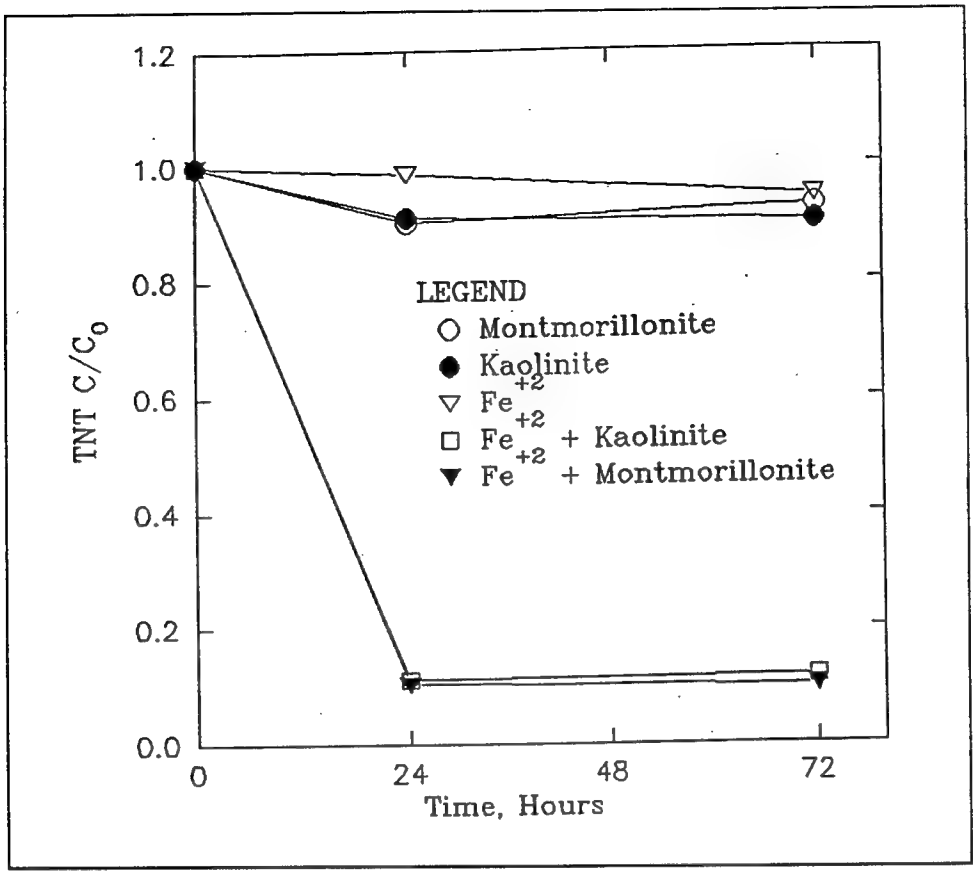

Figure 12. TNT in solution over time at each treatment versus concentration of TNT at sample time over initial concentration

disappearance in the treatments with clays or Fe^{+2} alone. No transformation products were detected in the treatments where TNT disappearance occurred. These results are consistent with the mechanism for transformation of nitroaromatics presented by Heijman et al. (1995) wherein Fe^{+2} sorbed to surfaces reduced a nitro group to an amino group. Following this reduction, TNT can form relatively insoluble and difficult to analyze azoxy compounds (Kaplan and Kaplan 1982). The disappearance of TNT and the detection of no degradation products support this mechanism of removal.

The rapid disappearance of TNT in the presence of Fe^{+2} sorbed to surfaces may explain the rapid disappearance of TNT from solution under highly reduced conditions (-150 mV). Reduction of Fe^{+3} to Fe^{+2} under highly reduced conditions is a rapid and continuing process (Gotoh and Patrick 1974). The sorbed Fe^{+2} so produced can then reduce TNT nitro groups to amino groups and Fe^{+3}. The Fe^{+3} formed as a result of the reduction reaction is rapidly reduced to Fe^{+2} under anaerobic conditions and the cycle continues.

4 Conclusions

TNT added to soils was more stable at lower pH, especially pH 5 under oxidizing to moderately reducing conditions. TNT was least stable at any pH under highly reduced conditions. Reduced soil conditions promoted rapid and complete disappearance of TNT. Soil component studies showed that the presence of Fe^{+2} sorbed to surfaces may explain the rapid disappearance of TNT from solution under highly reduced conditions (-150 mV). TNT persists at very low levels in soils only under moderately reducing and oxidizing conditions at pH 6 and below.

TNT in groundwater moving into an area of intense reduction would not long persist. The TNT would be rapidly transformed into mono and diamino compounds, which disappear from solution and soil. Soil extraction recovered only a small portion of the added TNT, and azoxy compounds were not found, indicating that the products of TNT degradation were bound to the soil in unknown, unextractable forms. Radiolabeled recovery tests showed that the labeled carbon was not mineralized but remained associated with the soil in some form.

References

Ainsworth, C. C., Harvey, S. D., Szecsody, J. E., Simmons, M. A., Cullinan, V. I., Resch, C. T., and Mong, G. H. (1993). "Relationship between the leachability characteristics of unique energetic compounds and soil properties," Final Report, U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.

Brannon, J. M. (1983). "The transformation, fixation, and mobilization of arsenic and antimony in contaminated sediments," Ph.D. diss., Louisiana State University, Baton Rouge, LA.

Cataldo, D. A., Harvey, S. D., Fellow, R. J., Bean, R. M., and McVeety, B. D. (1990). "An evaluation of the environmental fate and behavior of munitions material (TNT, RDX) in soil and plant systems: Environmental fate and behavior of TNT," Final Report, U.S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.

Folsom, B. L., Pennington, J. C., Teeter, C. L., Barton, M. R., and Bright, J. A. (1988). "Effects of soil pH and treatment level on persistence and plant uptake of 2,4,6-trinitrotoluene," Technical Report EL-88-22, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Gotoh, S., and Patrick, W. H., Jr. (1974). "Transformation of iron in a waterlogged soil as influenced by redox potential and pH," *Soil Sci. Soc. Amer. Proc.* 38, 66-70.

Heijman, C. G., Grieder, E., Holliger, C., and Schwarzenbach, R. P. (1995). "Reduction of nitroaromatic compounds coupled to microbial iron reduction in laboratory aquifer columns," *Environmental Science and Technology* 29, 775-783.

Kaplan, D. L., and Kaplan, A. M. (1982). "Mutagenicity of 2,4,6-trinitrotoluene by soils," *Bulletin of Environ. Contam. Toxicol* 28, 33-38.

Loganathan, P., and Burau, R. G. (1973). "Sorption of heavy metal ions by a hydrous manganese oxide," *Geochim. et Cosmochim. Acta.* 37, 1277-1293.

McCormick, N. G., Feeherry, F. E., and Levinson, H. S. (1976). "Microbial transformation of 2,4,6-trinitrotoluene and other nitroaromatic compounds," *Applied and Environmental Microbiology* 31, 949-958.

Nay, M. W., Randall, C. W., and King, P. H. (1974). "Biological treatability of trinitrotoluene manufacturing wastewater," *Journal of Water Pollution* 46, 485-497.

Palazzo, A. J., and Leggett, D. C. (1986). "Effect and disposition of TNT in a terrestrial plant," *Journal of Environmental Quality* 15, 49-52.

Patrick, W. H., Jr., Williams, B. G., and Moraghan, J. T. (1973). "A simple system for controlling redox potential and pH in soil suspensions," *Soil Science Soc. Am. Proc.* 37, 331-332.

Pennington, J. C., and Patrick, W. H., Jr. (1990). "Adsorption and desorption of 2,4,6-trinitrotoluene by soils," *Journal of Environmental Quality* 19, 559-567.

Pennington, J. C., Price, C. B., McCormick, E., and Hayes, C. A. (1992). "Effects of wet and dry cycles on TNT losses from soils," Technical Report EL-92-37, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Won, W. D., Heckly, R. J., and Hoffsommer, J. C. (1974). "Metabolic disposition of 2,4,6-trinitrotoluene," *Applied Microbiology* 27, 513-516.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	September 1995	Final report

4. TITLE AND SUBTITLE
Transformation of 2,4,6-Trinitrotoluene Under Controlled Eh/pH Conditions

5. FUNDING NUMBERS

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Engineer Waterways Experiment Station
3909 Halls Ferry Road, Vicksburg, MS 39180-6199;
AScI Corporation, 1701 Clay Street
Vicksburg, MS 39180-3020

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report
IRRP-95-5

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Corps of Engineers
Washington, DC 20314-1000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The presence of 2,4,6-trinitrotoluene (TNT) in soil and groundwater can present serious environmental problems. The processes that control the mobility and transformation of TNT in these environments are not well understood. The objective of this study was to determine the effects of redox potential (Eh) and pH on the transformation of TNT. Soil components responsible for the transformation of TNT were also investigated.

Laboratory investigations included testing at four different redox potentials and four pH levels. A 10:1 (water: soil) suspension spiked with 100 µg of TNT/g, dry weight soil was used. The aqueous phase was sampled over a 2-week period for TNT and its transformation products. Soils were analyzed at completion of the 2-week incubation period.

Results showed that redox potential and pH of the soil suspensions had a marked effect on TNT stability and transformation. The TNT was not stable under any Eh/pH conditions. TNT was least stable at any pH under highly reduced conditions. Results indicated that TNT persisted only under moderately reducing conditions and at lower pH levels. Soil component studies showed that the presence of Fe^{+2} sorbed to surfaces may explain the rapid disappearance of TNT from solution under highly reduced conditions (-150 mV). Radiolabeled TNT recovery tests in the

(Continued)

14. SUBJECT TERMS
pH
Redox potential
TNT transformation

15. NUMBER OF PAGES
29

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED		

13. (Concluded).

Eh/pH reactors showed that added TNT was not lost from the system in significant quantities. Soil extraction recovered only a small portion of the added TNT, and azoxy compounds were not found, indicating that the products of TNT degradation were bound to the soil in unknown and perhaps unextractable forms.

The data obtained in this study indicate that TNT in groundwater moving into an area of intense reduction would not persist. The TNT would be rapidly transformed into mono and diamino compounds, which disappear from solution and soil.

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